## Improvement of Cocoa-type Coatings for Use in Army Rations<sup>a</sup>

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A cocoa-type coating for use on confectionery rations that will withstand temperatures up to 49° C. (120° F.) for long periods of time and at the same time cannot be differentiated in palatability from regular fine chocolate coatings was developed. Previous use of these cocoa-type coatings made with fats of high melting points in the 49° C. (120° F.) range gave undesirable paraffin or waxy tastes. Low melting point fats were undesirable because of their tendency to bleed out, bloom and stick to the wrappers. Nonionic surface active agents "emulsifiers" were employed in the development of these new, stable, bloom resistant, and highly palatable summer type coatings. The vegetable fats with the emulsifiers added had a tendency to upgrade the melting points of these fats, i.e., these coatings could stand higher temperatures than the predetermined melting points of the vegetable fats used. On the other hand, the coating without the emulsifiers broke down at the temperature of the predetermined melting points of the vegetable fats used. The addition of non-fat milk solids to the coating was found to aid in the palatability also. Another advantage of the added emulsifiers is that they keep the coating from sticking to the wrappers and eliminate the greasy feeling associated with the use of hydrogenated vegetable fats.

The extensive use of fats and oils in confectionery products for the Armed Forces of the United States has naturally caused more attention to be focused on the structure of these fats. The Quartermaster Corps has been interested from the standpoint of the shelf life of coated candy bars used in various rations. This paper on cocoa-type coatings is the result of cooperative research of the General Products Division of the Quartermaster Food and Container Institute and the Research Laboratories of the Paul F. Beich Company.

The number and types of fats and oils are indeed impressive and we shall limit ourselves to natural vegetable oils and fats used in coatings for candy bars. These vegetable oils and fats are mixtures of triglyceryl esters of the fatty acids. An oil or fat by itself usually contains a number of these esters in various percentages. Chemically there is very little difference between fats or oils, although physically, there are differences; oils are liquid at low tempertures, fats are liquid at high temperatures. The term "fats" in this article implies solid or liquid triglycerides (oils or fats).

In the use of these fats in confections, especially in the production of coatings, the melting points and softening agents are very important. It must be borne in mind

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that, whether these fats are natural or hydrogenated, they are mixtures of various glycerides and usually do not show sharp melting points. Therefore, the term "melting point" does not imply the same characteristics that it does with pure substances of a definite crystalline nature. Fats first gradually soften and shrink in volume before they become completely liquid. Many wonder why there is a difference in melting and softening points observed by chemists working in separate laboratories. The reason for this is that an analyst can duplicate his own results if he uses his own uniform procedure, but there are many variables in procedures for fat analysis. The melting point must be defined by the specific conditions by which it has been determined and is usually the temperature at which the fat becomes perfectly clear and liquid, whereas the softening point is the temperature at which the fat softens or becomes sufficiently fluid to slip or run. The capillary tube, open tube, and the Wiley methods are used for determining softening or melting points. The melting points referred to in this paper were determined by the Wiley and open tube methods, which are described in any standard food analysis text (3) or the Official and Tentative Methods of the American Oil Chemists' Society.

The cocoa butter used in chocolate is especially suitable for coating because it possesses a comparatively low melting point which is very much sharper than most fats in this low range. Also, in the solid state it is somewhat brittle and not very greasy to the touch. This is due to the particular physical and chemical properties of the glyceride structure of the fat, i.e., the high percentage of monooleodisaturated glycerides. Don't be alarmed as this is not an article on the component glycerides of natural fats. The chemistry of the saturated and the unsaturated fatty acids is very complicated. There are many excellent texts (2) on edible fats and oils that go into physical and chemical properties, classification, etc., if one is interested in this phase of chemistry.

The Armed Forces require cocoa-type coatings which will stand up for long periods of time at temperatures up to 49° C. (120° F.) for use in desert and tropic areas. These coatings must not only remain stable in these high temperatures and not stick to the wrappers, but must be palatable and nutritive as well. Previous use in these cocoa-type coatings of fats with softening or melting points in the 49° C. (120° F.) range, which will not melt at body temperature, gave an undesirable paraffin or shortening taste (1). The use of low melting point fats which bleed out in hot weather resulted in a grey, unpalatable, sticky coating. Even though agents could be added to cocoa butter in regular chocolate coatings to cause them to resist a limited amount of heat, the very low melting point of cocoa butter causes it to bleed at relatively low temperatures.

In order to make the "summer-type" coatings "hardened" oils are used. These hardened oils are hydrogenated vegetable fats which are made by passing hydrogen through the heated oils in presence of a suitable catalyzer, usually under pressure. These fats have heat-resistance properties and their eating qualities are very much improved by hydrogenation. These hydrogenated fats undergo a complete change in chemical and physical properties.

In the development of a stable coating for candy bars, we started by testing the properties of these hydrogenated vegetable fats that are used in summer coating with combinations of various surface active agents or emulsifiers. Non-ionic surface active agents which we will call emulsifiers were employed in the development of a stable summer-type coating. These emulsifiers are complex esters or ester-ethers, their chemical starting points being hexahydric or polyhydric alcohol esters which may be fatty acid esters of glycerol, sorbitol, glycols, etc. These non-ionic surface active agents do not ionize in water as do the anionic and cationic surface active agents.

To select the most useful and desirable emulsifier for chocolate-type coatings, the answer lies in the correct hydrophilic-lipophilic combination which must also have the best general chemical and physical properties that will be compatible with the various components that make up the coatings. Hydrophilic (polar) means water-loving, water-attracting or water-soluble and lipophilic (non-polar) means fat-loving, fat-attracting or fat-soluble. It is possible for an emulsifier to love fat and not hate water and vice versa. Unlike human love, the emulsifier love can be weighed and be expressed in numbers.

Generally the hydrophilic character of the emulsifier is supplied by the free hydroxyl and oxyethylene groups, while the lipophilic portion is found in the long aliphatic carbon atom chain of the fatty acid or fatty alcohol. The emulsifiers in any ester range will vary in freezing points, melting points, have wax-like or oily properties, vary in solubility or dispersibility, etc. Thus, the emulsifiers not only emulsify, but can disperse, suspend, and thicken coatings.

The above outline on the general properties of emulsifiers will indicate the problem in picking out the best single or combination of emulsifiers to be added to the coating with hydrogenated vegetable fats to overcome the problems that have been encountered previously. In our work we felt that a certain hydrophilic-lipophilic balance was necessary for the emulsifiers to be used, also, their physical and chemical properties had to be satisfactory and also be compatible with the various components of the coating. We were searching for a combination which would be polygamous (poly—much, plus gamos—married). Yes, a polygamous emulsifier

which could be married to every component of the coating.

First we started with the following vegetable fats from high lauric sources as they have been shown from previous tests to have the best properties from the standpoint of resisting rancidity.

Vegetable Fat	Melting Point, ° F.	Softening Point, " F.
X	114.36 to 120	99
Y	108 to 113	97.7
Z	98.8	86

With these vegetable fats Y & Z with different predetermined melting points and softening points were incorporated various percentages and combinations of emulsifiers and these were observed at high temperatures and high relative humidities.

Many emulsifiers and combinations of emulsifiers were rejected because of their physical or chemical properties, some gave the coating a bitter or rancid taste or turned rancid on shelf-life tests, and others were too oily or waxy. Many were rejected since they showed no evidence of improvement of coatings. Therefore, we are listing only the combinations of emulsifiers which gave us the many improvements we were seeking in a coating for the Armed Forces. The list of emulsifiers used included the following:

Span 60 (sorbitan monostearate, S60),<sup>b</sup>
Span 65 (sorbitan tristearate, S65),
Tween 60 (polyoxyethylene sorbitan monostearate, T60),<sup>b</sup>
Tween 65 (polyoxyethylene sorbitan tristearate, T65),
G1086 (polyoxethylene sorbitol hexaoleate),
PG400M (polyethylene glycol 400 monostearate),<sup>c</sup>
C1000M (Carbo-wax 1000 monostearate),
MGM (monoglycerol monostearate), and Lecithin.

Used in combinations or alone, these emulsifiers indicated the following order of effectiveness in improving the resistance to heat:

No. 1. 1% of a 50-50 mixture of S60 and T60,

No. 2. 0.25% S60, 0.25% T60 and 0.1% G1086,

No. 3. 1% of a 60-40 mixture of S60 and T60,

No. 4. 1% of a 50-50 mixture of S65 and T65,

No. 5. 0.5% of PG400M and 0.5% C1000M,

No. 6. 0.1% MGM and 0.3% lecithin, and

No. 7. 0.5 lecithin.

The Y coating with lecithin or mono glycerol stearate (No. 6 or No. 7) will pass the old QM standards when used in summer coating that is, to withstand 38° C. (100° F.) for two hours and when cooled to 21° C. (70° F.) for one hour will not stick to the wrapper. By the addition of 1% of a 50-50 mixture of Span 60 and Tween 60 (No. 1) to the Y cocoa-type coating it will upgrade this fat to stand up for 96 hours at 49° C. (120° F.). Y coatings without these emulsifiers will break down under such conditions.

<sup>&</sup>lt;sup>b</sup> Trademarks of Atlas Powder Co.

<sup>&</sup>lt;sup>e</sup> Manufactured by the Emulsol Corp. and Glyco Co.

Similarly, by the addition of 1% 50-50 Span 60 and Tween 60 to coatting Z it will upgrade this fat to pass the old QM test as used in a summer coating although in a 96-hour test at 38° C. (100° F.) it will begin to break down. The coating without emulsifiers will not meet the old QM test and breaks down completely at 96 hours at 38° C. (100° F.).

Number 2 almost equaled the performance of No. 1; it did show a lowering in viscosity due to G1086. G1086, being an oleate, needs further study as oleates have a tendency to turn rancid on storage. Number 3 and No. 4 gave good results but were not equal in overall performance to No. 1 or No. 2.

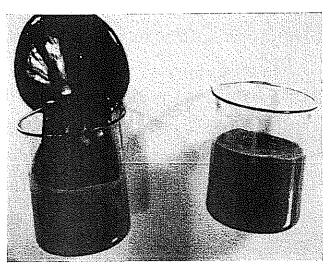
Number 5 showed some improvement over No. 6 and No. 7, but did not compare with No. 4. The above tests were run on summer-type coating having the following formula:

Cocoa powder (10% cocoa fat)	7.5%
Fat (all vegetable)	32.0%
Vanillin (1 oz.)	0.0625%
Spans 60	0.5%
Tweens 60	0.5%
Sugar	59.4375%

It is a known fact that non-fat milk solids increase the shelf life of summer-type coating and produce a coating free of the shortening taste. Production formulas for two types of summer coating with non-fat milk solids found in the new QM specifications are as follows:

Component	Dark-sweet type percent by weight	Light-sweet type percent by weight
Cocoa powder (10-14% cocoa fat)	not less than 17.5 not less than 12.0 not less than 31.0 not more than 0.2 0.5	not less than 7.5 not less than 12.0 not less than 30.0 not more than 0.2 0.5
Polyoxyethylene sorbitan monostearate Sugar	0.5 not more than 38.0	0.5 not more than 49.0
Salt (per 100 pounds of coating)	not more than 2 oz.	not more than 2 oz.

To summarize the above results, it was found that combinations No. 1 or No. 2 of emulsifiers produced an unusual and unexpected result. The vegetable fats with the emulsifiers added had a tendency to upgrade the melting points of these vegetable fats, i.e., these coatings would stand higher temperatures than the predetermined melting points of the vegetable fats used. On the other hand, the coating without the emulsifiers broke down at the temperature of the predetermined melting points of the vegetable fats used. The addition of nonfat milk solids to the cocoa-type coating resulted in confections which not only withstood higher temperatures, but at the same time eliminated the waxy, shortening taste. Even though the melting point of the fats used in the cocoa-type coating is higher than body temperature, the emulsifiers tend to incorporate this fat into a creanly mass which when eaten with the centers of the various bars, produces a very palatable and nutritive type confection. Another advantage is that these emulsifiers prevent the coating from sticking to the wrappers and



F16. 1. Ten seconds flow of QM type coating from beakers placed horizontally after coating had been subjected to 120° F. for 96 hours. Left: prepared with emulsifiers (1% of a mixture of 50-50 Span 60 and Tween 60; right: prepared without emulsifiers.

eliminate the greasy feeling that is so often associated with the use of hydrogenated vegetable fats.

This upgrading effect which withstands the higher temperatures is no doubt due to the correct polygamoshydrophilic lipophilic balance emulsifiers. It loves and tolerates water, fat, protein, and at the same time disperses, suspends, and thickens. It is a polygamous "shotgun" wedding.

Thus the shelf life and palatability of Quartermaster cocoa-type coatings have been improved and these improvements have been incorporated in the new revision of Quartermaster specifications on confectionery products.

Since these improvements on cocoa type coatings, tests were also under way to improve the moulded Enriched Sweet Chocolate Discs as they do not have the necessary shelf-life requirements. Generally, up to 3% cocoa butter can be added to hydrogenated coconut oil coating without effecting gloss or texture of the finished confection. The No. 1 emulsifier combination as used in cocoa type coatings gave the improvements necessary to incorporate the high percentage of cocoa butter found in the chocolate liquor when used with hydrogenated coconut fats. The following formula of a chocolate type coating for moulded Enriched Chocolate Disc meets the rigid Quartermaster requirements.

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Sugar	50.33%
Hydrogenated coconut oil	16.60%
(110-114° F. m.p., Wiley)	
Whole milk solids	16.00%
Chocolate liquor (54% cocoa butter)	
Span 60.	0.5%
Tween 60	
Thiamine chloride, 12 mg. per oz.	
Thiamine chloride, 12 mg. per oz.	

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